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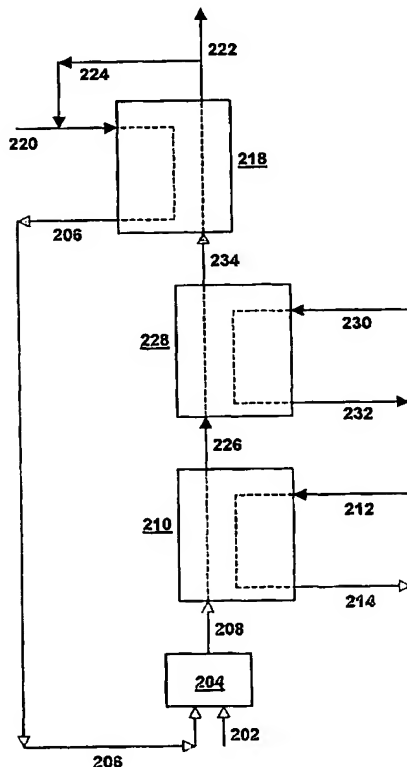
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[Continued on next page]

(54) Title: PROCESS FOR THE EXTRACTION OF ENERGY FROM FLUE GASES



(57) Abstract: The invention relates to a process for the extraction of energy from flue gases of a furnace which is operated with a fuel (202) and which is used in a process for the production of melamine, the process comprising a first heat exchange step (210) in which the flue gases are heat exchanged with a first process stream (212, 232), and in which the flue gases are heat exchanged with a second process stream (230, 232) in a second heat exchange step (228). The invention also relates to an apparatus for supplying heat in a process for the preparation of melamine, and to a process for optimizing an existing apparatus.



European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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PROCESS FOR THE EXTRACTION OF ENERGY FROM FLUE GASES

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The invention relates to a process for the extraction of energy from flue gases of a furnace which is operated with a fuel and which is used in a process for the production of melamine, the process comprising a first heat exchange step in which the flue gases are heat exchanged with a first process stream.

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Such a process is known and is applied in many processes for the production of melamine. In the known process the furnace is a salt furnace. Fresh air and natural gas as fuel are supplied to burners. In the combustion of natural gas with the fresh air flue gases are formed. In the first heat exchange step the flue gases are heat exchanged with a first process stream, i.e. molten salt. In order to achieve a higher energy efficiency, energy is additionally extracted in the known process from the flue gases by means of heat exchange with fresh air; the heated air is subsequently fed to the burners of the furnace. Through the said heat exchange with fresh air the overall energy efficiency rises to approximately 90%. Energy efficiency is defined as the percentage of the energy released in the combustion of fuel that is absorbed by a particular stream or streams or by a total of streams.

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The known process has the disadvantage that the heated air fed to the furnace leads to increased NO_x emission in comparison with a furnace in which the fresh air is not preheated. The increase in NO_x emission as a result of the heated fresh air is observed with all types of burner. The undesired increase in NO_x emission can admittedly be limited by separating a proportion of the flue gases, combining that proportion with fresh air and thus heating a mixture of fresh air and recirculated flue gases and feeding it to the burners of the furnace. Nevertheless, the NO_x emission remains undesirably high; the NO_x emission in the flue gases of the known process is generally 110 mg/Nm³ or higher. As is known, the unit Nm³ stands for the volume of a gas under standardized conditions of pressure and temperature. These conditions are 273K and 0.1013 MPa.

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It is the object of the present invention to lessen the said disadvantage and yet achieve a higher energy efficiency than the energy efficiency of the said heat exchange with molten salt.

The said object is attained by the flue gases being heat exchanged in a second heat exchange step with a second process stream.

5 An advantage of the process according to the invention is that the NO_x emission decreases in comparison with the known process, while the combination of the first with the second heat exchange step allows energy to be efficiently extracted from the flue gases.

A furnace here means a furnace which is heated essentially with the aid of combustion; the fuels will in practice usually be natural gas or oil, although the process according to the invention is not limited thereto.

10 The furnace is used in a process for the production of melamine. "Use" means that the energy which is released in the furnace is used as process heat. An example of an application of process heat is heating the reactor in which melamine is prepared from urea in an endothermic reaction.

15 A process for the production of melamine here refers to any possible process. Examples of known processes for the production of melamine are described in for example Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition, 2001, Chapter 'Melamine and Guanamines', section 4.

20 Flue gases here refers to combustion gases resulting from the combustion of a fuel such as natural gas or oil. The flue gases have a high temperature, usually of 600°C to 800°C to 1000°C, or even up to 1200°C or higher.

The embodiment of the heat exchange which is carried out in the first or second heat exchange steps according to the invention, is known per se, such as in a heat exchanger. Heat exchange may be direct; this means that the flue gases exchange heat with the process stream to be heated via at the most a fixed partition.
25 Heat exchange may also be indirect; this means that the flue gases exchange heat with a heat transfer medium, after which the heat transfer medium is heat exchanged with the process stream to be heated in a separate heat exchange step. Examples of heat transfer media are molten salt, Dowtherm® and steam.

30 A process stream here refers to a stream which is used or consumed in a process for the production of melamine. Examples of a process stream are: feedstock streams such as urea; auxiliary streams such as ammonia, air in a pneumatic transport system, molten salt, Dowtherm, steam, boiler feedwater; reactor effluent and all downstream streams such as off-gases, melamine slurry, wet melamine crystals; sidestreams such as mother liquor. Fresh air for combustion in the furnace
35 does not fall under the definition of a process stream. The first and second process

streams as meant in the process according to the invention will in general be two different process streams; however, they may also be one and the same stream.

In order to obtain a high energy efficiency from the said first and second heat exchange steps it will usually be necessary to cool the flue gases to a relatively low temperature, for example to 350°C to 300°C or lower, say, 250°C or even to 200°C or lower. This can be accomplished using processes known per se. An example of this is a combination of successive heat exchange steps with each subsequent heat exchange step delivering energy to a process stream at a lower temperature level. An example of such a combination of heat exchange steps is the heating in the first heat exchange step of molten salt from approximately 420°C to approximately 450°C, followed by the heating in the second heat exchange step of ammonia from approximately 150°C to approximately 400°C. Another example of such a combination of the first and the second heat exchange steps is heating molten salt from approximately 420°C to approximately 450°C, followed by the heating of Dowtherm from 200°C to 350°C. A further example of such a combination of the first and the second heat exchange steps is heating ammonia from approximately 250°C to approximately 450°C, followed by heating urea from approximately 135°C to approximately 250°C. By choosing the correct combination of heat exchange steps, in conjunction with choosing the correct embodiments of the heat exchange steps, for example by means of countercurrent instead of cocurrent heat exchange, the temperature of the flue gases can fall to such an extent that the energy efficiency in the process according to the invention is higher than 85%, preferably higher than 88%, more preferably higher than 90%, still more preferably higher than 92%, most preferably higher than 94%. An energy efficiency up to 99.5% will be possible, although this will require considerable effort; an efficiency up to 99% or 97% or 96% will therefore often be accepted in practice.

The NO_x emission in the process according to the invention decreases in comparison with the known process; the emission can decrease to less than 100 mg/Nm³, preferably less than 95 mg/Nm³, more preferably less than 90 mg/Nm³, most preferably less than 85 mg/Nm³, measured according to Clause 4 of the "Besluit emissie-eisen stookinstallaties milieubeheer A' (Order stating emission requirements for combustion installations environmental management A'), also known as BEES (version valid from 23-11-2000, Dutch Bulletin of Acts and Decrees 2000, 443). In order to achieve the said emission values it may be necessary, in addition to the implementation of the process according to the invention, to optimize in terms NO_x

emission the design in general and burners in particular, in a way known per se to one skilled in the art.

The aforesaid emission values do not imply that preheating fresh air through heat exchange with flue gases, as practiced in the known process, is altogether impossible in the process according to the invention. This is because it is advantageous if there is, besides the energy extraction in the first and second heat exchange steps according to the invention, still another possibility for further energy extraction. Therefore, the process according to the invention preferably also comprises a third heat exchange step for the flue gases with fresh air; here the NO_x emission in the flue gases is preferably less than 100 mg/Nm³. Compliance with specified emission values does entail that preheating fresh air with the aid of the flue gases must be limited in such a way that the stated emission values are not exceeded. This can be accomplished by limiting the temperature increase of the fresh air. This can lead to a situation where it is necessary to limit the energy efficiency resulting from preheating fresh air to less than 15% or 10%, preferably to less than 8% or 6%, or to less than 5% or 4%. In that case, but also if preheating fresh air is not applied, it may additionally be advantageous, as in the known process, to separate a proportion of the flue gases, to mix that proportion with fresh air and thus feed a mixture of fresh air and recirculated flue gases to the burners.

Preheating the fresh air with the flue gases by means of the third heat exchange step may be effected before, during or after the first or the second heat exchange steps with the first and the second process stream. If the fresh air is preheated prior to the first or the second heat exchange step, it is important to carefully verify that the energy efficiency and NO_x emission remain within the limits indicated above. Therefore, the fresh air is preferably preheated during or after the first or the second heat exchange steps, most preferably after the second heat exchange step.

The furnace is preferably a salt furnace. A salt furnace here means a furnace in which salt is melted via the first heat exchange step, if that had not been done yet, and is heated, after which the molten salt serves to supply process heat in a process for the production of melamine, so that there is mention here of indirect heat exchange. Such salt furnaces are known per se. In salt furnaces employed in a process for the production of melamine the molten salt from the process usually enters the furnace at a temperature of between 400°C and 440°C, in order to be heated to 450°C or higher. As a result, after heat exchange with the molten salt, the flue gases

usually still have a temperature of approximately 400°C or higher; this temperature then is the inlet temperature for the second heat exchange step.

In a preferred embodiment the process according to the invention comprises a first heat exchange step with molten salt, followed by a second direct heat exchange step with a process stream which consists essentially of ammonia. As is known, ammonia is used and/or consumed in various places in processes for the production of melamine. In some of these places it is necessary for the ammonia to have a high temperature above 300°C, often approximately 350°C to 400°C or higher up to approximately 450°C. Examples hereof are the use of ammonia as the fluidization gas in the reactor of a gas-phase process for the production of melamine, or the use of ammonia in the reactor of a high-pressure liquid-phase process. In practice, heat exchange with steam is inadequate for heating ammonia to the said values, since ammonia heat exchanged with industrially available steam can in general be heated to no more than 200°C to 250°C. This means that the ammonia must be heated further by a different method; examples of known different methods are electrical heating of pipelines carrying the ammonia to be heated, or the use of a heat exchange step with molten salt. The said known methods for heating ammonia further up to the said values are technically complex and indirect and so of relatively low efficiency. An advantage of the process according to the invention is that heat exchange between the flue gases and ammonia in the second heat exchange step makes possible a direct and efficient, energy-saving, technically simple and economically favourable temperature increase of ammonia to 300°C to 400°C or more. The ammonia to be heated may be gaseous, liquid or in supercritical condition. Preferably the ammonia to be heated is liquid or in supercritical condition, because heat exchange to a liquid or supercritical medium is technically simpler to implement than heat exchange to a gaseous medium.

In another preferred embodiment the process according to the invention comprises a first heat exchange step with molten salt, followed by a second direct heat exchange step with a process stream which consists essentially of urea. It is known from high-pressure melamine production processes that urea can be heated by bringing the urea in direct contact with gases released in the reaction of urea to form melamine and which gases are usually eventually returned to a process for the preparation of urea. In addition to this, however, there may still be a need for an additional method for heating urea, for example in a non-steady state of the plant such as during start-up; also, the known process is not generally applicable in low-pressure

processes for the production of melamine. It is therefore advantageous for urea to be used as the process stream in the process according to the invention.

The industrial applicability of the process according to the invention is to be found amongst other things in salt furnaces commonly used in practice. The invention therefore also relates to an apparatus for supplying process heat in a process for the production of melamine, comprising a salt furnace which includes a heat exchange unit in which salt is heated; the first heat exchange step is carried out herein. The apparatus according to the invention contains at least one further heat exchange unit which directly or indirectly heats a process stream: the second heat exchange step is carried out herein. The presence of the at least one further heat exchange unit which heats a process stream contributes to achieving an energy efficiency of 85% or more, without the need to preheat fresh air. Preferably the further heat exchange unit is a heat exchange unit for the direct heating of ammonia or urea. In addition it is preferable, having due regard to the NO_x emission requirements as previously stated, to provide the apparatus also with a heat exchange unit for heating fresh air; the third heat exchange step is carried out herein.

The industrial applicability of the process according to the invention is further to be found in the optimization of an existing apparatus for the supply of process heat in a process for the production of melamine. Application of the process according to the invention can be realized in an existing apparatus by adding at least one heat exchange unit for the direct or indirect heating of a process stream. The addition of the at least one further heat exchange unit which heats a process stream contributes to achieving an energy efficiency of 85% or more without having to rely for this on preheating fresh air. Preferably the added heat exchange unit is then used for the direct heating of a process stream which consists essentially of ammonia or urea. If the existing apparatus includes a heat exchange unit for preheating fresh air, the added heat exchange unit is preferably positioned such that the flue gases first pass through the added heat exchange unit before the flue gases preheat fresh air. Since fresh air extracts less energy and is thus preheated to a lesser extent, the NO_x emission of the existing apparatus will decrease, with the eventually achieved emission value being dependent on the specific conditions of the existing apparatus.

In practice it is often desirable that a process stream, such as a heat transfer medium or an auxiliary stream such as ammonia, is at the same time available at various temperature levels. Since the heat exchange steps with a process stream must be dimensioned to supply the highest desired temperature level to the process for

the production of melamine, there is thus a need to provide a possibility of supplying that process stream also at a lower temperature level to the process for the production of melamine. In a preferred embodiment of the process according to the invention there is therefore applied a fourth heat exchange step in which a process stream is heat
5 exchanged with the flue gases, with the process stream supplied to the fourth heat exchange step having a higher temperature than the flue gases supplied to the fourth heat exchange step. An example of such a fourth heat exchange step is first separating a proportion of a stream of molten salt which is supplied to, or discharged from, the first heat exchange step, followed by supplying to the fourth heat exchange step the
10 separated stream of molten salt, with the flue gases, because of the second and possibly the third heat exchange step, having decreased in temperature such that the flue gases in the fourth heat exchange step are heated and the molten salt is cooled.

An advantage of this fourth heat exchange step, which leads to the flue gases being reheated somewhat, is that condensation upon final emission of the
15 flue gases can be prevented. A further advantage is that the design of the unit in which this separate fourth heat exchange step is carried out is simpler than when the heat transfer medium must be discharged during the first or second heat exchange with the flue gases.

In the process according to the invention it is well possible to
20 introduce, in addition to the above-mentioned heat exchange steps, a fifth or further heat exchange steps with a process stream. This will depend on the specific circumstances of the case, such as for example the presence and heating requirements of the process streams present. An embodiment is also possible which does not include the third heat exchange step.

25 The invention is elucidated with reference to the drawings described hereinafter.

In the drawings Figure 1 shows an embodiment of the prior art, in which a fuel and fresh air are supplied to a burner; the flue gases are successively heat
exchanged with molten salt and with fresh air.

30 Figure 2 shows an embodiment according to the invention, in which the flue gases pass through two heat exchange steps with process streams before heat is exchanged with fresh air.

Figure 3 shows an embodiment according to the invention, in which the flue gases, following heat exchange with molten salt, a process stream and with

fresh air, are reheated somewhat by heat exchange with a proportion of the molten salt.

The first digit of the numbers in the figures is the same as the number of the figure. Where the last two digits of the numbers of different figures are the same, they refer to the same component.

5 In Fig. 1 natural gas is supplied via line 102 to burner 104, where the natural gas is combusted with the aid of combustion air supplied via 106. Flue gases are formed in this process. The flue gases are conveyed through duct 108 to heat exchanger 110, where the flue gases are heat exchanged with molten salt supplied
10 through line 112 and, once heated, discharged through line 114. The flue gases are then supplied through duct 116 to heat exchanger 118, where the flue gases are heat exchanged with fresh air. The fresh air is supplied via line 120, and, after heating, discharged through 106 as combustion air to burner 104. The flue gases are discharged through duct 122. In order to achieve flue gas NO_x reduction a proportion of
15 the flue gases is recirculated via 124 by mixing with the fresh air supplied through 120.

In Fig. 2, in comparison with Fig. 1, the flue gases, following heat exchange with a process stream (such as molten salt) are passed through 210 not directly to a heat exchange step with fresh air but first through duct 226 to heat exchanger 228. In 228 the flue gases exchange heat again with a process stream (for
20 example supercritical ammonia) supplied via line 230 and, after heating, are discharged via line 232. Next, the flue gases are supplied through duct 234 to heat exchanger 218.

In Fig. 3, in comparison with Fig. 2, the flue gases, after heat exchange with fresh air in 318, are supplied through duct 322 to heat exchanger 336;
25 here the flue gases are heat exchanged with a proportion of the process stream that had been discharged through 314; this partial stream is supplied via line 338. As a consequence of heat exchange in 336 the flue gases will be reheated somewhat, and the process stream will cool somewhat. The cooled process stream is discharged via 340; the flue gases through duct 342.

30 The invention is further elucidated with reference to an example and a comparative experiment.

Example I

35 An apparatus according to Fig. 2 in which the process according to the invention is applied comprises a salt furnace. The first heat exchange step of the

flue gases is carried out with molten salt in heat exchanger 210; the second heat exchange step with gaseous ammonia in heat exchanger 228; the third heat exchange step of the flue gases is carried out with fresh air in heat exchanger 218. A proportion of the flue gases is separated and mixed with fresh air via 224.

5 The salt furnace is heated by means of combustion, in burner 204, of 1625 Nm³/h natural gas with a mixture of approximately 90 vol.% fresh air and approximately 10 vol.% recirculated flue gases with a total volume of 20,850 Nm³/h. The molten salt, approximately 500 m³/h, is heated from 414°C in line 212 to 450°C in line 214. The gaseous ammonia, approximately 22,500 kg/h, is heated from 210°C in
10 line 230 to 250°C in line 232. The mixture of fresh air and recirculated flue gases is heated in heat exchanger 218 from 32°C to 158°C. The flue gases eventually emitted through 222 have a temperature of 220°C.

The overall energy efficiency is 91%; the NO_x emission is 80 mg/Nm³.

15 Comparative experiment

An apparatus according to the state of the art, see Fig. 1, comprises a salt furnace. The flue gases are heat exchanged with molten salt in heat exchanger 110. There is no further direct or indirect heat exchange with a process stream. But the flue gases are eventually heat exchanged with fresh air in heat exchanger 118. A
20 proportion of the flue gases is separated and mixed with fresh air via 124.

The salt furnace is heated by means of combustion, in burner 104, of 1625 Nm³/h natural gas with a mixture of approximately 90 vol.% fresh air and approximately 10 vol.% recirculated flue gases with a total volume of 20,850 Nm³/h. The molten salt, approximately 500 m³/h, is heated from 414°C in 112 to 450°C in 114.
25 The mixture of fresh air and recirculated flue gases is heated in 120 from 47°C to 398°C in 106. The flue gases that are ultimately emitted via 122 have a temperature of 125°C.

The overall energy efficiency is 93%; allowance should be made here for the fact that in the apparatus according to the state of the art no ammonia stream
30 has been heated as in Example I; this will require a separate heat exchange step in the process for the production of melamine, for example by means of steam or through electrical heating of the line carrying the ammonia to be heated, which has a negative effect on the efficiency given here. Also, in this embodiment the flue gases are cooled to a lower temperature, which leads also to a higher efficiency. The NO_x emission is
35 100 mg/Nm³.

As appears from Example I and the comparative experiment, with the process according to the invention a high energy efficiency can be combined with a low NO_x emission.

CLAIMS

1. Process for the extraction of energy from flue gases of a furnace which is operated with a fuel and which is used in a process for the production of melamine, the process comprising a first heat exchange step in which the flue gases are heat exchanged with a first process stream, characterized in that the flue gases are heat exchanged with a second process stream in a second heat exchange step.
2. Process according to claim 1, further comprising a third heat exchange step in which the flue gases are heat exchanged with fresh air.
3. Process according to claim 1 or 2, wherein the furnace is a salt furnace.
4. Process according to claim 3, wherein in the first heat exchange step the flue gases exchange heat with molten salt, and wherein in the second heat exchange step the flue gases exchange heat with a process stream which consists essentially of ammonia.
5. Process according to claim 3, wherein in the first heat exchange step the flue gases exchange heat with molten salt, and wherein in the second heat exchange step the flue gases exchange heat with a process stream which consists essentially of urea.
6. Process according to claim 1 or 2, comprising a fourth heat exchange step in which a process stream is heat exchanged with the flue gases, with the process stream which is supplied to the fourth heat exchange step having a higher temperature than the flue gases which are supplied to the fourth heat exchange step.
7. Apparatus for supplying process heat in a process for the production of melamine, comprising a salt furnace which includes a heat exchange unit in which salt is heated, characterized in that the apparatus includes at least one further heat exchange unit which directly or indirectly heats a process stream.
8. Apparatus according to claim 6, which includes as further heat exchange unit a heat exchange unit for the direct heating of a process stream which consists essentially of ammonia or urea.
9. Apparatus according to claim 6 or 7, which further contains a heat exchange unit for heating fresh air.
10. Process for optimizing an existing apparatus for the supply of process heat from flue gases in a process for the production of melamine, characterized in

that at least one heat exchange unit is added for the direct or indirect heating of a process stream.

11. Process according to claim 9, in which the added heat exchange unit is used for the direct heating of a process stream which consists essentially of ammonia or urea.

Figure 1/3

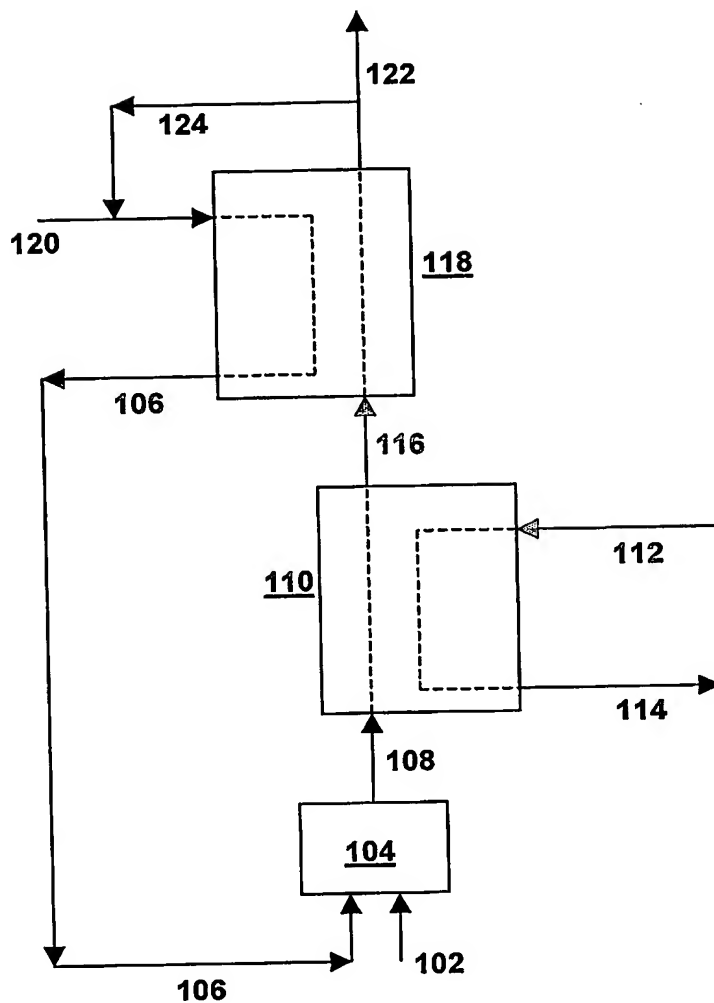


Figure 2/3

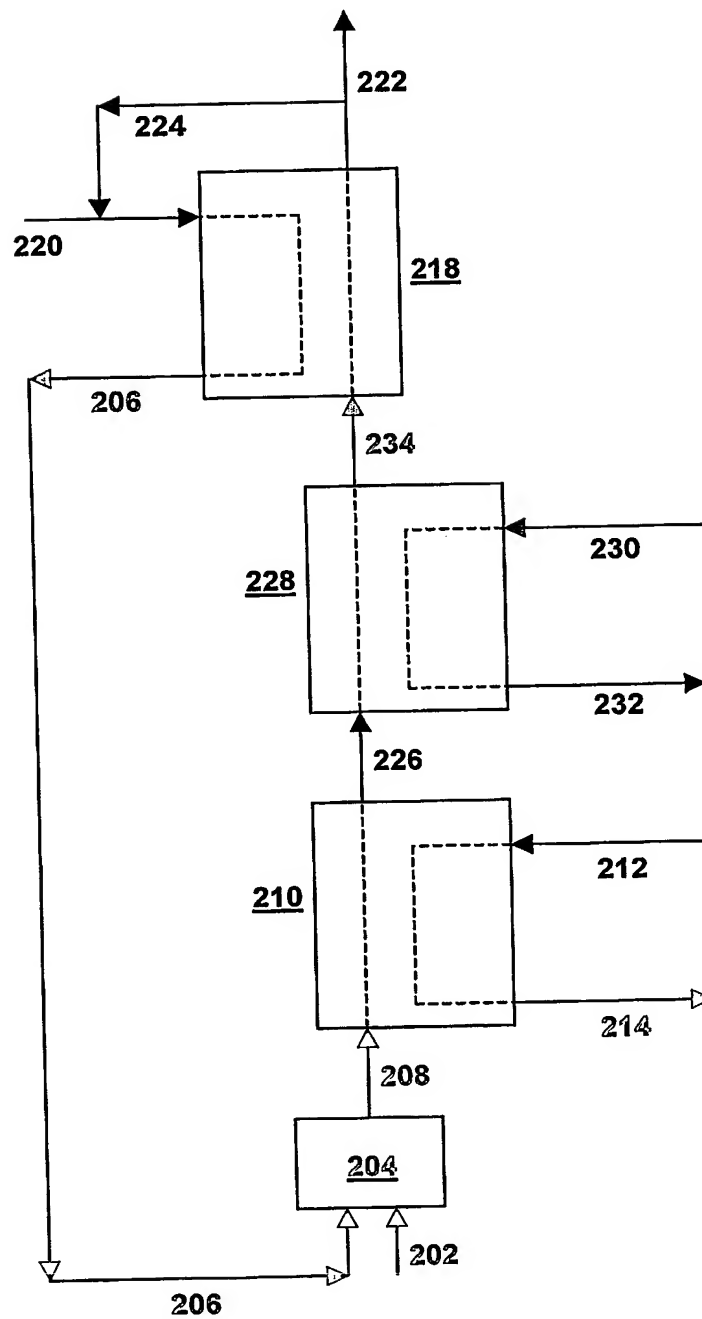
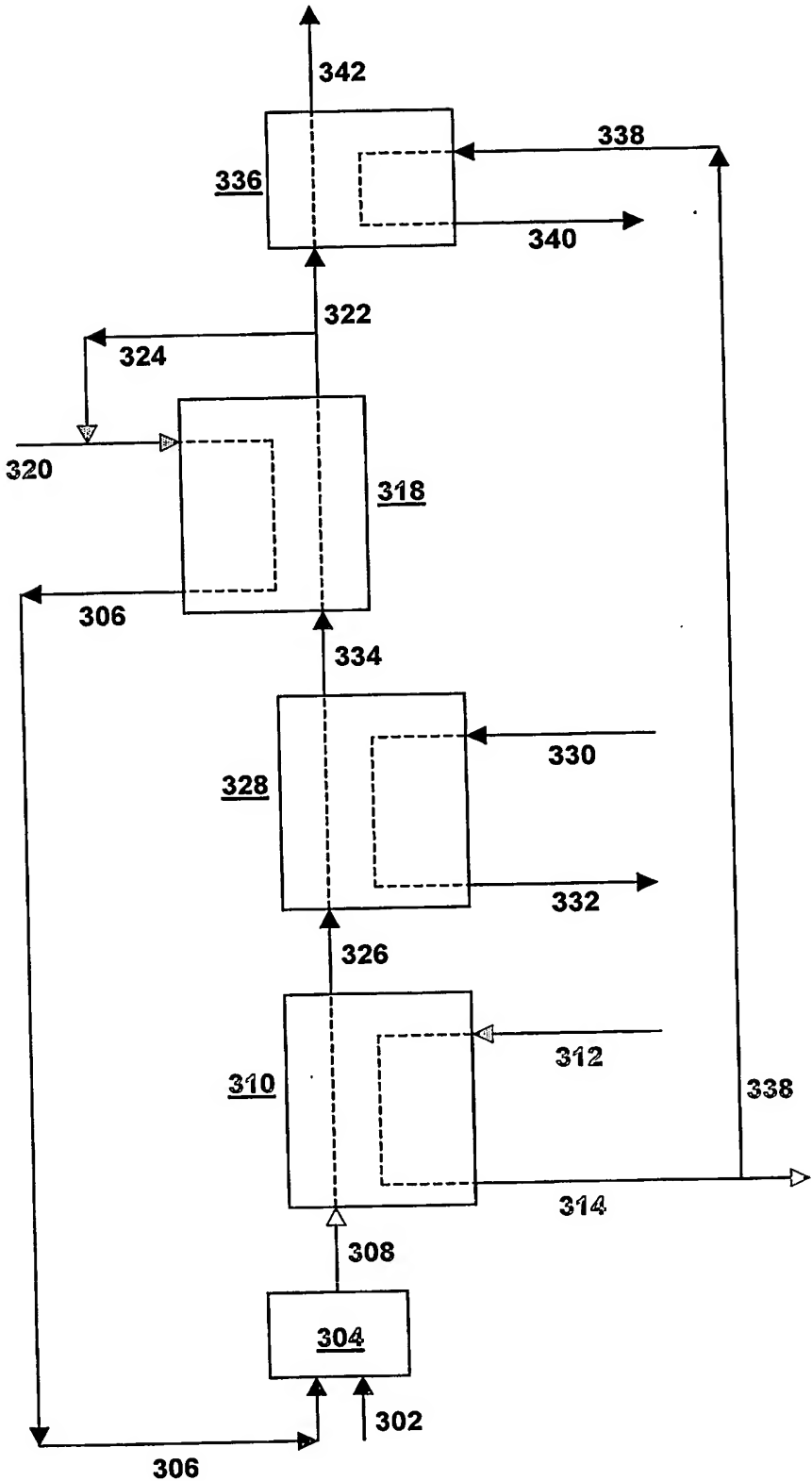


Figure 3/3



INTERNATIONAL SEARCH REPORT

Internat'l Application No
PCT/NL 03/00897

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 F28D21/00 C07D251/56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 F28D F23L C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	GB 2 182 395 A (FOSTER WHEELER ENERGY LTD) 13 May 1987 (1987-05-13) page 1, line 16 - line 24 page 2, line 38 -page 3, line 7; figures	1,3,7,10
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A	DE 889 749 C (AMERICAN CYANAMID COMPANY NEW) 14 September 1953 (1953-09-14) the whole document	1,7,10
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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